

# PATENT ABSTRACTS OF JAPAN

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## (54) INK COMPOSITION

### (57)Abstract:

PURPOSE: To form an invisible and highly water-resistant printed image by including a solution comprised of a dendrimer and a dye contg. a porphyrin chromophore in the ink composition.

CONSTITUTION: A solution is obtained by solving 0.0005–0.01 wt.% a dye contg. a porphyrin chromophore, 0.01–15 wt.% a dendrimer, 0–70 wt.% wetting agent and 0.0001–4 wt.% a fungicide in a liq. vehicle consisting of 100–30 wt.% water and 0–70 wt.% a water-soluble org. component. An ink composition is prepared by keeping the solution at 10–30° C, stirring it at 20–25° C for 2–24 hours, filtering it and then regulating pH of the solution at 6.5–10.5 by dropping an acid.

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**CLAIMS**

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[Claim(s)]

**[Claim 1] An ink constituent containing a solution containing a color and DIN DORIMA containing a porphyrin chromophore.**

[Detailed Description of the Invention]

**[0001]**

**[Industrial Application]** This invention relates to an ink constituent, its image formation, and the printing method. furthermore, printing of the image with which, as for this invention, it was concealed the object for secrecy, or for encodings in one embodiment by details -- setting -- the effective quick-drying fluorescence ink constituent for ink jets -- it is -- ink -- a porphyrin chromophore or a relative -- it is related with the ink constituent containing the color and DIN DORIMA based on a component, or its mixture.

**[0002]**

**[Description of the Prior Art]** These colors have a band very strong against 380 - 500 nanometers of an absorption spectrum, and a Soret band, and there is a very weak band in a 600 -800-nanometer range further. Moreover, these colors show fluorescence in the 600 - 800-nanometer range, and this spectral range differs from the luminescence aperture property of the optical brightener used in commercial paper. In one embodiment, the ink of this invention contains a porphyrin chromophore color like tetra-pyridinium porphyrin TETORAASETETO, the aqueous solution vehicle which contains a solvent depending on the case, and DIN DORIMA. Water, After mixing DIN DORIMA and a color, water and the auxiliary solvent containing a glycol like a diethylene glycol can be added, and ink can be prescribed. The potential time amount which is the maximum time amount for which an ink jet print head without the lid which may deteriorate the injection engine performance remarkably is not used by this

For example, less than 1 hour, about 1 - Are improvable in about 10 minutes. This addition Ink drying time, That is, when another paper sheet in the case of handling is made to contact and it places, the duration which dries an ink jet print to the degree which dirt is not attached and is not offset can be improved, and it is this drying time less than 1 minute, for example Especially about 0.2 - It is about 5 seconds. Moreover, it is ink viscosity when a glycol is added About 1.1 - It is about 1.1 preferably about 5 centipoises. - It can adjust to about 3.0 centipoises and the surface tension of ink can be adjusted.

[0003] In order that that the homogeneity of the print which has sharpness, the print of the minimum [ blot / the ink in the paper ], and the ink coverage of for example, a poor region is desirable may form the print of the feature in the edge between the quality print which was usually excellent in the paper, i.e., the edge sharpness which can be permitted, a print area, and a non-printed region, viscosity and surface tension are the main contribution factors. The ink of this invention can be used by the known ink jet print processes of many like the thermal ink jet method indicated by U.S. Pat. No. 4,601,777, 4,251,824, 4,410,899, 4,412,224, and 4,532,530 or Bubble Jet. Furthermore, in details, the ink of this invention can be used in order to form the image which cannot be viewed, and it can be viewed according to special observation conditions which irradiate ultraviolet rays to a specific user at an image. These images are detectable also by sensor like a fluorescence detector.

[0004] The fluorescence ink of this invention is effective in especially printing of the image with which it was concealed for secrecy like printing of a document including the information which only the limited reader was allowed. As for the ink of this invention, it is effective to perform marking which cannot be viewed on a document again especially in the method for which it asks. in order to control the number which copies a document as an example of such a condition, the machine which performs marking which can detect with the image-formation equipment which performs safety marking, and orders image-formation equipment, and which cannot view and with which the document of an original copy was made identifies -- it is -- it is -- the perfect form of printing \*\*\*\* controls -- it is -- it is -- it may act as a monitor on the lower stream of a river of functional actuation Including the fluorescent dye as which these ink was chosen from many colors besides DIN DORIMA, these colors have the special solvent mixed liquor and the compatibility with which giving the ink of quick dry like 0.2 to 5 seconds is known, when it injects in a clerical work form. At quick-drying and the outstanding water resisting property, and an embodiment, it is about 90. - About 99% is effective like the connected document as a rapid object for printing which is printed the speed for 50-100 copy/with a xerography. Moreover, in an embodiment, the ink of this

invention has water stain resistance. Generally the ink jet printing method can be classified into two kinds known as a continuous injection system and a drop method on demand.

[0005]

[Problem(s) to be Solved by the Invention] This invention is offering the ink constituent which has many advantages explained on these descriptions. Another object of this invention is offering the constituent for ink jets containing a specific color and specific DIN DORIMA.

[0006]

[Means for Solving the Problem] It is attained by offering an ink constituent containing these aqueous solution vehicles of this invention with which other objects contain a specific color and specific DIN DORIMA in the embodiment by reaching. In one embodiment, ink of this invention contains a solution containing a porphyrin mold color and DIN DORIMA. As a suitable porphyrin mold color for ink of this invention For example, a 5, 10, 15, 20-tetrakis-(1-methyl-4-pyridyl)-21H, and 23H-porphin tetra--p-tosylate salt (Aldrich Chemical Corporation make), A 5, 10, 15, 20-tetrakis-(1-methyl-4-pyridyl)-21H, and 23H-porphin tetra-chloride salt, A 5, 10, 15, 20-tetrakis-(1-methyl-4-pyridyl)-21H, and 23H-porphin tetra-bromide salt, A 5, 10, 15, 20-tetrakis-(1-methyl-4-pyridyl)-21H, and 23H-porphin tetra-acetate salt, A 5, 10, 15, 20-tetrakis-(1-methyl-4-pyridyl)-21H, and 23H-porphin tetra-pel chlorate salt, 5, 10, 15, 20-tetrakis-(1-methyl-4-pyridyl)-21H, and 23H-porphin tetrafluoroborate, A 5, 10, 15, 20-tetrakis-(1-methyl-4-pyridyl)-21H, and 23H-porphin tetra-pel chlorate salt, A 5, 10, 15, 20-tetrakis-(1-methyl-4-pyridyl)-21H, and 23H-porphin tetra-triflate salt, A 5, 10, 15, 20-tetrakis-(1-hydroxymethyl-4-pyridyl)-21H, and 23H-porphin tetra--p-tosylate salt, A 5, 10, 15, 20-tetrakis-[1-(2-hydroxyethyl)-4-pyridyl]-21H, and 23H-porphin tetra-chloride salt (For example, it prepares as indicated by V.N.Madakyan, Chemistry of Heterocyclic Compounds, 1986, and page 167-171) [0007] A 5, 10, 15, 20-tetrakis-[1-(3-hydroxypropyl)-4-pyridyl]-21H, and 23H-porphin tetra--p-tosylate salt, A 5, 10, 15, 20-tetrakis-[1-(2-hydroxypropyl)-4-pyridyl]-21H, and 23H-porphin tetra--p-tosylate salt, A 5, 10, 15, 20-tetrakis-[1-(2-hydroxy ethoxyethyl)-4-pyridyl]-21H, and 23H-porphin tetra--p-tosylate salt, A 5, 10, 15, 20-tetrakis-[1-(2-hydroxy ethoxy propyl)-4-pyridyl]-21H, and 23H-porphin tetra--p-tosylate salt, A 5, 10, 15, 20-tetrakis-[4-(trimethylammonio) phenyl]-21H, and 23H-porphin tetra--p-tosylate salt (Aldrich Chemical Corporation make), A 5, 10, 15, 20-tetrakis-[4-(trimethylammonio) phenyl]-21H, and 23H-porphin tetra-chloride salt, A 5, 10, 15, 20-tetrakis-[4-(trimethylammonio) phenyl]-21H, and 23H-porphin tetra-bromide salt, A 5, 10, 15, 20-tetrakis-[4-(trimethylammonio) phenyl]-21H, and 23H-porphin tetra-

tetra-acetate salt, A 5, 10, 15, 20-tetrakis-[4-(trimethylammonio) phenyl]-21H, and 23H-porphin tetra-pel chlorate salt, 5, 10, 15, 20-tetrakis-[4-(trimethylammonio) phenyl]-21H, and 23H-porphin tetrafluoroborate, 5, 10, 15, 20-tetrakis-[4-(trimethylammonio) phenyl]-21H, and 23H-porphin tetra-triflate salt, [0008] Meso-(N-methyl-X-pyridinium) n-(phenyl)4-n-21H and 23H-porphin tetra--p-tosylate salt (n is the integer of 0, 1, 2, or 3) X=4-p and 3-m Or 2-o expresses a location of nitrogen of a pyridinium substituent. For example, Biochemistr(ies), such as M.A.Sari, 1990, 29,; meso-tetrakis-[o-(N-methylnicotinamide) phenyl]-21H that are prepared as indicated by 4205-4215, and 23H-porphin tetramethyl sulfonate salt (for example, G.M.Miskelly etc.) Inorganic Chemistry, a 1988, 27,;5 that are prepared as indicated by 3773-3781, 10 and 15, 20-tetrakis-(2-sulfonate ethyl-4-pyridyl)-21H, and 23H-porphin chloride salt (it Yotsuyanagi(s) S. -- Igarashi and T. --) A Chemistry Letters, 1984,;5 that are prepared as indicated by 1871, 10 and 15, 20-tetrakis-(carboxymethyl-4-pyridyl)-21H, and 23H-porphin chloride salt, A 5, 10, 15, 20-tetrakis-(carboxy ethyl-4-pyridyl)-21H, and 23H-porphin chloride salt, A 5, 10, 15, 20-tetrakis-(carboxy ethyl-4-pyridyl)-21H, and 23H-porphin bromide salt, a 5, 10, 15, 20-tetrakis-(carboxylate-4-pyridyl)-21H, and 23H-porphin bromide salt (it Arnold(s) D. -- P. --) Australian Journal of Chemistry, 1989, 42, and 2265-2274;2, 3, 7, 8, 12, 13 and 17, 18-OKUTA-(2-hydroxyethyl)-21H, and 23H-porphin prepared as indicated, 2, 3, 7, 8, 12, 13, 17, 18-OKUTA-(2-hydroxy ethoxyethyl)-21H, and 23H-porphin, 2, 3, 7, 8, 12, 13, 17, 18-OKUTA-(2-aminoethyl)-21H, and 23H-porphin, 2, 3, 7, 8, 12, 13 and 17, 18-OKUTA-(2-hydroxy ethoxy propyl)-21H, and 23H-porphin etc. is mentioned. These colors can also come to hand and many are Organic Synthesis, A.I.Meyers, Editor, Volumes 70, and 68-72 (1991). It can also prepare with a known means like general composition indicated.

[0009] A liquefied vehicle of ink of this invention Various known components, for example, water, water, and glycols for example, ethylene glycol, propylene glycol, and a diethylene glycol -- A glycerol, dipropylene glycol, a polyethylene glycol, a polypropylene glycol, An amide, the ether, a carboxylic acid, ester, alcohol, the ORGANO sulfide, The ORGANO sulfoxide, a sulfone, dimethyl sulfoxide, a sulfolane, Mixed liquor with a miscibility organic component like an alcoholic derivative, carbitol, butyl carbitol, Cellosolve, an ether derivative, amino alcohol, and a ketone; water miscibility matter besides germicide;, its mixed liquor, etc. can be included. a ratio [ as opposed to / when using mixed liquor of water and a water miscibility organic liquid like a glycol as a liquefied vehicle / an organic liquid of water ] -- a scope -- it is -- typical -- about 100:0 - about 30:70 -- desirable -- about 97:3 - it is referred to as about 50:50. Generally, non-water or an organic component of a liquefied vehicle with the boiling point higher

than water (100 degrees C) acts as a wetting agent. A liquefied vehicle component, for example, water, and a wetting agent of ink have an absorption property and an evaporation property over paper, and when ink should be used in ink jet print processes, they can take into consideration a desired ink jet print speed. It is related with ink of this invention in an embodiment, and is a liquefied vehicle About 85 - It is about 90 preferably about 99.5% of the weight. - It can be made to exist in about 99% of the weight of an amount.

[0010] An additive of arbitration can also be made to exist in ink of this invention, as shown by this description. For example, one or more sorts of surfactants, wetting agents, or dispersants can be added in ink. There is a cation, an anion, both sexes, or an ion mold in these additives. As a suitable surfactant, a wetting agent, or a dispersant A TAMOL(registered trademark) SN, TAMOL(registered trademark) LG, and TRITON (registered trademark) system (product made from Rohm and Haas Company), MARASPERSE A system (registered trademark) and an IGEPAL (registered trademark) system (product made from GAF Company), TERGITOL (registered trademark) A system and STRODEX PK-90 (registered trademark) (product made from GAF), PLURONIC F-68 (registered trademark) (BASF make) and KARASPERSE TU (registered trademark) (product made from Marasperse) And a surfactant of other marketing is mentioned. these surfactants and wetting agents -- a scope of arbitration -- usually -- about 0 - about 15 % of the weight -- desirable -- about 0.01 - it is made to exist at about 8 % of the weight In order to raise the viscosity of ink, it is an effective dose, 1 [ for example, ], about a macromolecule additive or a dispersant. - It can also add in ink of this invention at about 15 % of the weight. As an example, gum arabic, a polyacrylate salt, a polymethacrylate salt, Polyvinyl alcohol, hydroxypropylcellulose, hydroxyethyl cellulose, Polyvinyl pyrrolidinone, polyvinyl ether, starch, polysaccharide, Sodium salt of a naphthalene sulfonate formaldehyde copolymer, Water-soluble polymer, such as sodium salt of sodium salt of alkylbenzene sulfonate, sodium salt of dialkyl sulfo succinate, sodium salt of lignosulphonate, a sodium alkylene oxide copolymer, and alkyl ether phosphate, is mentioned. Furthermore, hydroxypropyl polyethyleneimine (HPPEI-200) Or polymer like other polyethyleneimine derivatives can also be added in ink. In an effective dose of arbitration, and a type target, it is a macromolecule stabilizer to ink of this invention 0 - It is about 0.01 preferably about 10% of the weight. - It can be made to exist at about 5 % of the weight.

[0011] an injection property and storage stability of ink are improved, or it is an injection process -- it is -- as other additives of arbitration prevented so that ink and a print head may not carry out an interaction which is not desirable while a printer is not using ink of this invention, as this description explained Ethylene glycol, a diethylene

glycol, N-methyl pyrrolidinone, Propylene glycol, the hydroxy ether, the ether, an amide, a sulfoxide, Wetting agents, such as a ketone, lactone, ester, and alcohol (0 - about 50% of the weight) It is about 5 preferably. - It is made to exist in about 40% of the weight of an amount.; DOWICIL (registered trademark)75, germicides (an effective dose --), such as 150 and 200, a benzoate salt, and a sorbate salt for example, about 0.0001 - about 4 % of the weight -- desirable -- about 0.01 - it is made to exist at about 2.0 % of the weight -- and an acid or a base -- PH regulators (0 [ - It is about 4 preferably about 10% of the weight. / - It is made to exist in about 8% of the weight of an amount. ] - it is about 0.01 preferably about 5% of the weight - making it existing in about 2% of the weight of an amount, a base is 0), such as a phosphate salt, a carboxylate salt, a SURUFAITO salt, and an amine salt, etc. are mentioned.

[0012] DIN DORIMA was combined with initiation nuclei, such as nitrogen and ethylenediamine, and a nucleus -- for example Each arm includes a repeating unit including 3 or four arms. STARBURST including the functionality of an end functional group like a primary amine combined with an internal layer and a outermost part product by which it is considered that a repeat factor of each arm is the product of DIN DORIMA (registered trademark) A radial symmetrical molecule of a topology gestalt can be considered. For example, U.S. Pat. No. 4,507,466, 4,631,337, In 4,558,120, 4,568,737, and a 4,587,329 list, D.A.Tomalia, A. M.Naylor, W.A.GoddardIII, Angewandte Chemie, and Int.Ed.Engl.29,138 (1990) It is illustrated. STARBURST (registered trademark) DIN DORIMA shown on these descriptions [ like ] -- usually -- about 0.05 - about 10 % of the weight -- desirable -- about 1 - in order to make it exist with an effective dose like about 5% of the weight of concentration and to obtain a transparent solution -- water -- it is preferably mixed with distillation or water by which deionization is carried out.

[0013] An ink constituent of this invention is suitable to use it by ink jet print processes like continuation injection, a piezo-electric drop on demand, bubble jet, or a thermal ink jet method. A method of building ink of this invention into an ink jet airline printer, making a drop of ink inject to an image pattern on a suitable base generally, and making an image form on a base is included. In order to make an image form with an ink constituent indicated on these descriptions, it is DIABLO C150IJ (registered trademark). A printer and Hewlett Packard DESK JET (registered trademark) A printer and DIABLO C150 TIJ (registered trademark) Various known ink jet equipments, such as a printer, are used. Especially a thermal ink jet airline printer is desirable. A regular paper like Xerox4024 paper, and GILBERT (registered trademark) 25% cotton bond paper or GILBERT (registered trademark) In order to make an image form on a base of versatility, such as a bond paper like a 100% cotton bond paper, a silica

coated paper, a transparent material, a fabric, plastics, and a high polymer film, ink of this invention can be used.

[0014] In an embodiment, ink of this invention can make possible a printing document which brown can usually be slightly presented from yellow in many cases, and a color containing a porphyrin chromophore can function as an indicator agent, and can be detected according to special observation conditions. As for ink of this invention, it is effective to perform marking which cannot be viewed on a document in a method for which it asks. As an example of such a condition Image formation equipment which controls a number which performs safety marking and copies a document can detect, and it orders image formation equipment. A case where a machine with which a document of an original copy which performs marking which gives (for example, an instruction into which it is made not to copy a particular part of a document, or a color of a particular part of a document is changed), and which cannot be viewed was made is identified etc. is mentioned. An example of equipment or a machine which can be used, and its specific ink is the United States Patent \*\*\*\*\* under simultaneous connection. It is indicated by 07/636,246 (D/89191) number. Furthermore, ink containing two or more sorts of colors which a visible wavelength range is colorlessness and can be detected by method using one sort or several sorts of sensors in other wavelength regions is effective. An image is irradiated using an ink constituent containing a solution which contains a color containing a porphyrin chromophore in an embodiment of this invention, and its certification method, for example, the light source emitted by 300 - 450 nanometers, and a printing method of a concealed image detectable [ with fluorescence including detecting light taken out to a 500 -800 nanometer spectral range by image using a sensor with sensitivity ] is included.

[0015] An ink constituent of this invention can be prepared by various suitable methods. Typically, a component is mixed simply and ink is prepared. One embodiment is the method of mixing all components of ink, filtering mixed liquor, and obtaining ink. It is mixed liquor obtained after mixing all components depending on the case About 40 - It can heat to temperature of about 55 degrees C for about 2 to 3 hours, the mixed liquor can be successingly cooled to a room temperature (it is about 10 typically - about 35 degrees C), the mixed liquor can be filtered, and ink can be obtained. Furthermore, an aqueous solution of (1) color is added to details at a mechanical stirring aqueous solution of DIN DORIMA, a wetting agent, and a germicide, and it is a color 0.0005 [ about ]. - About 0.01 % of the weight, It is about 0.001 preferably. - They are about 0.008 % of the weight and DIN DORIMA 0.01 [ about ]. - About 15 % of the weight, It is about 0.1 preferably. - They are about 2 % of the weight and a wetting agent 0 [ about ]. - It is about 3 preferably about 70% of the weight. - About 50 % of the weight, Germicide

0.0001 [ about ] - It is about 0.01 preferably about 4% of the weight. - They are about 2 % of the weight and \*\*\*\* 29.5. - About 99.5 % of the weight, It is about 49.5 preferably. - A solution containing about 96.5 % of the weight is generated. This solution Ten to 30 degree C, Mixed liquor which maintained at temperature of 20 to 25 degree C preferably, and was; (2) Obtained is stirred at temperature of 20 to 25 degree C for 2 to 24 hours. Depending on the; case Mixed liquor which could heat this mixed liquor from 30 minutes at temperature of 30 to 60 degree C for 2 hours, and was; (3) Obtained is filtered with 0.45micro filter.; (4) acid, For example, it is Omega by dropping an aqueous solution of a hydrochloric acid or an acetic acid. Ink of this invention can be prepared by adjusting to ink pH 6.5-10.5 measured with a pH meter.

[0016]

[Example 1] An ink constituent was prepared as follows. Cyclohexyl pyrrolidinone (product made from AldrichChemical Corporation) 5.0g, Butyl carbitol (Aldrich Chemical Corporation make) 21.0g, Glycerol (Aldrich Chemical Corporation make) 14.0g, Polyethylene oxide (MW 18,500, product made from Polysciences) 0.08g, DOWICIL 200 (registered trademark) (product made from Dow Corporation) 128 mg and 195.52g of deionized water were mixed at a room temperature and about 25 degrees C, and a stock solution was prepared. This solution was stirred with a magnetic agitator for 3 hours. It is STARBURST (registered trademark) in 33.0g of this solution. DIN DORIMA of the 1st product (Michigan Molecular Institute make) A 0.87 ml 5, 10, 15, 20-tetrakis-(1-methyl-4-pyridyl)-21H, and 23H-porphin tetra--p-tosylate salt (6.1mg, product made from Aldrich Chemical Corporation) which dissolved in 1.104ml of aqueous solutions and 10ml of water 10% of the weight was added. This mixed liquor was filtered with 0.45micro filter. 0.005 % of the weight of porphyrin colors, 0.3 % of the weight of DIN DORIMA, 83.7 % of the weight of water, 8.4 % of the weight of butyl carbitols, 5.6 % of the weight of glycerol, 2 % of the weight of cyclohexyl pyrrolidinone, 0.032 % of the weight of polyethylene oxide, and DOWICIL (registered trademark) Brown ink containing 0.05 % of the weight was obtained.

[0017] In this way, prepared ink was included in a DESK JET Hewlett Packard (registered trademark) ink jet printer. Xerox 4024 paper (Xerox Corp. make) and Sanyo KokusakuFX-L A print was formed on paper (Fuji Xerox make). A pattern was undetectable on a print under observation conditions ordinary about each. Macbeth TR927 Optical density of a poor print area measured with a concentration meter was 0.02. Fluorolog 212 When a print put into a sample room of fluorescence spectrometer (product made from SPEX) was irradiated on wavelength of 418 nanometers, light was emitted in strong fluorescence characterized by 648 nanometers and two bands of max 714 nanometers. Contrast excellent in both papers was acquired. It is related with

Xerox4024 paper and is the fluorescence intensity (648 nanometers) of a print area. Fluorescence intensity of a blank paper (648 nanometers) A receiving ratio is 10 and is Sanyo Kokusaku FX-L. About paper, it was 11.7. A print area described Xerox 4024 paper (a wire side) was cut on a sheet of two sheets, one sheet was immersed in water for 2 minutes, this immersed sheet was air-dried at a room temperature for 24 hours, and the water resisting property of a print for which it asked by measuring fluorescence intensity which irradiated both an immersed sheet and a sheet which is not immersed under the same conditions was 85.6% (0.83 / 0.97x100).

[0018]

[Example 2] Ink of contrast was prepared as follows. Cyclohexyl pyrrolidinone (product made from AldrichChemical Corporation) 5.0g, Butyl carbitol (Aldrich Chemical Corporation make) 21.0g, Glycerol (Aldrich Chemical Corporation make) 14.0g, Polyethylene oxide (MW 18,500, product made from Polysciences) 0.08g, DOWICIL 200 (registered trademark) (product made from Dow Corporation) 128 mg and 195.52g of deionized water were mixed at a room temperature and about 25 degrees C, and a stock solution was prepared. This solution was stirred with a magnetic agitator for 3 hours. 5, 10, 15, 20-tetrakis-(1-methyl-4-pyridyl)-21H, and 23H-porphin tetra--p-tosylate salt which dissolved in 33.0g of this solution at 1.104ml of water, and 10ml of water (6.1mg, product made from Aldrich Chemical Corporation) 0.87ml of solutions was added. This mixed liquor was filtered with 0.45micro filter. A presentation of this ink was substantially [ as ink indicated in the example 1 ] the same except not containing DIN DORIMA. A water resisting property indicated to be what indicated a physical characteristic in the example 1 about viscosity and surface tension at this ink in this example although it was substantially the same was low.

[0019] Prepared ink was included in a DESK JET Hewlett Packard (registered trademark) ink jet printer. Xerox 4024 paper (Xerox Corp. make) and Sanyo Kokusaku FX-L A print was formed on paper (Fuji Xerox make). A pattern was undetectable on a print under observation conditions ordinary about each. Macbeth TR927 Optical density of a poor print area measured with a concentration meter was 0.03. Fluorolog 212 When a print put into a sample room of fluorescence spectrometer (product made from SPEX) was irradiated on wavelength of 418 nanometers, light was emitted in strong fluorescence characterized by 648 nanometers and two bands of max 714 nanometers. Contrast excellent in both papers was acquired. About Xerox 4024 paper, a ratio to fluorescence intensity (648 nanometers) of a blank paper of fluorescence intensity (648 nanometers) of a print area is 10, and is Sanyo Kokusaku FX-L. About paper, it was 11.7. A print area described Xerox 4024 paper (a wire side) was cut on a sheet of two sheets, one sheet was immersed in water for 2 minutes, this immersed sheet was air-dried at a

room temperature for 24 hours, and the water resisting property of a print for which it was asked by measuring fluorescence intensity which irradiated both an immersed sheet and a sheet which is not immersed under the same conditions was 35.7% (0.34 / 0.95x100).

[0020]

[Example 3] An ink constituent was prepared as follows. Cyclohexyl pyrrolidinone (product made from AldrichChemical Corporation) 5.0g, Butyl carbitol (Aldrich Chemical Corporation make) 21.0g, Glycerol (Aldrich Chemical Corporation make) 14.0g, Polyethylene oxide (MW 18,500, product made from Polysciences) 0.08g, DOWICIL 200 (registered trademark) (product made from Dow Corporation) 128 mg and 195.52g of deionized water were mixed at a room temperature and about 25 degrees C, and a stock solution was prepared. This solution was stirred with a magnetic agitator for 3 hours. It is STARBURST (registered trademark) in 33.0g of this solution. DIN DORIMA of the 1st product (Michigan Molecular Institute make) A 0.87 ml 5, 10, 15, 20-tetrakis-(4-trimethyl aminophenyl)-21H, and 23H-porphin tetra--p-tosylate salt (5.9mg, product made from Aldrich Chemical Corporation) which dissolved in 1.104ml of aqueous solutions and 10ml of water 10% of the weight was added. This mixed liquor was filtered with 0.45micro filter. 0.005 % of the weight of porphyrin colors, and STARBURST (registered trademark) 0.3 % of the weight (Michigan Molecular Institute make) of DIN DORIMA, 83.7 % of the weight of water, 8.4 % of the weight of butyl carbitols, 5.6 % of the weight of glycerol, 2 % of the weight of cyclohexyl pyrrolidinone, 0.032 % of the weight of polyethylene oxide, and DOWICIL (registered trademark) of the 1st product Brown ink containing 0.05 % of the weight was obtained.

[0021] In this way, prepared ink was included in a DESK JET Hewlett Packard (registered trademark) ink jet printer. Subsequently, Xerox 4024 paper (Xerox Corp. make) and Sanyo Kokusaku FX-L A print was formed on paper (Fuji Xerox make). A pattern was undetectable on a print under observation conditions ordinary about each. Macbeth TR927 Optical density of a poor print area measured with a concentration meter was 0.03. Fluorolog 212 When a print put into a sample room of fluorescence spectrometer (product made from SPEX) was irradiated on wavelength of 418 nanometers, light was emitted in strong fluorescence characterized by 650 nanometers and two bands of max 715 nanometers. Contrast excellent in both papers was acquired. About Xerox 4024 paper, a ratio to fluorescence intensity (648 nanometers) of a blank paper of fluorescence intensity (648 nanometers) of a print area is 9, and is Sanyo Kokusaku FX-L. About paper, it was 11.2. A print area described Xerox 4024 paper (a wire side) was cut on a sheet of two sheets, one sheet was immersed in water for 2 minutes, this immersed sheet was air-dried at a room temperature for 24 hours, and the

water resisting property of a print for which it asked by measuring fluorescence intensity which irradiated both an immersed sheet and a sheet which is not immersed under the same conditions was 88.4% (0.84 / 0.95x100).

[0022]

[Example 4]

A preparation porphyrin color [ of a porphyrin color ] 5, 10, and 15, 20-tetrakis-(2-hydroxyethyl-4-pyridyl)-21H, and 23H-porphin chloride salt was prepared as follows. 5, 10, 15, 20-tetrakis-(pyridyl)-21H, and 23H-porphin (product made from Aldrich Chemical Company) 2.0g was added to 2-chloroethanol 100ml put into a 200ml round bottom flask furnished with a reflux capacitor and a magnetic agitator. The heating reflux of this mixed liquor was carried out for 5 hours. Vacuum distillation of the cooled reaction mixed liquor was carried out, and a solvent was removed. The desiccation residue was washed by diethylether 500ml. Filtration separated this and it recrystallized with 10 % of the weight of water, and 750ml of mixed liquor of 90 % of the weight of propanol. A refined product (2.47g, 83% of yield) was a purple-brown solid. As for a visible absorption spectrum (IR) of this underwater matter, a band with 420 nanometers strong [ a center ] and 516 nanometers, and 584 nanometers showed two central weak bands.

[0023]

[Example 5]

An ink preparation ink constituent was prepared as follows. Cyclohexyl pyrrolidinone (product made from AldrichChemical Corporation) 5.00g, Butyl carbitol (Aldrich ChemicalCorporation make) 21.0g, Glycerol (Aldrich Chemical Corporation make) 14.0g, Polyethylene oxide (MW 18,500, product made from Polysciences) 0.08g, DOWICIL 200 (registered trademark) (product made from Dow Corporation) 128 mg and 195.52g of deionized water were mixed at a room temperature and about 25 degrees C, and a stock solution was prepared. This solution was stirred with a magnetic agitator for 3 hours. It is STARBURST (registered trademark) in 9.0g of this solution. DIN DORIMA of the 1st product (Michigan Molecular Institute make) 0.11ml of solutions of a 5, 10, 15, 20-tetrakis-(2-hydroxyethyl-4-pyridyl)-21H, and 23H-porphin tetra-chloride salt (what was prepared by 4.46mg and the above) which dissolved in 0.08ml of aqueous solutions and 2ml of water 10% of the weight was added. This mixed liquor was filtered with 0.45micro filter. 0.005 % of the weight of porphyrin colors, 0.3 % of the weight of DIN DORIMA, 84 % of the weight of water, 8.4 % of the weight of butyl carbitols, 5.6 % of the weight of glycerol, 2 % of the weight of cyclohexyl pyrrolidinone, 0.032 % of the weight of polyethylene oxide, and DOWICIL (registered trademark) Brown ink containing 0.05 % of the weight was obtained.

[0024] In this way, prepared ink was included in a DESK JET Hewlett Packard (registered trademark) ink jet printer. Xerox 4024 paper (Xerox Corp. make) and Sanyo KokusakuFX-L A print was formed on paper (Fuji Xerox make). A pattern was undetectable on a print under observation conditions ordinary about each. Macbeth TR927 Optical density of a poor print area measured with a concentration meter was 0.03. Fluorolog 212 When a print put into a sample room of fluorescence spectrometer (product made from SPEX) was irradiated on wavelength of 418 nanometers, light was emitted in strong fluorescence characterized by 654 nanometers and two bands of max 717 nanometers. Contrast excellent in both papers was acquired. About Xerox4024 paper, a ratio to fluorescence intensity (654 nanometers) of a blank paper of fluorescence intensity (654 nanometers) of a print area is 10.2, and is Sanyo Kokusaku FX-L. About paper, it was 12. A print area described Xerox 4024 paper (a wire side) was cut on a sheet of two sheets, one sheet was immersed in water for 2 minutes, this immersed sheet was air-dried at a room temperature for 24 hours, and the water resisting property of a print for which it asked by measuring fluorescence intensity which irradiated both an immersed sheet and a sheet which is not immersed under the same conditions was 94.8% (0.93 / 0.98x100).

[0025]

[Example 6] An ink constituent was prepared as follows. Cyclohexyl pyrrolidinone (product made from AldrichChemical Corporation) 5.00g, Butyl carbitol (Aldrich ChemicalCorporation make) 21.0g, Glycerol (Aldrich Chemical Corporation make) 14.0g, Polyethylene oxide (MW 18,500, product made from Polysciences) 0.08g, DOWICIL 200 (registered trademark) (product made from Dow Corporation) 128 mg and 195.52g of deionized water were mixed at a room temperature and about 25 degrees C, and a stock solution was prepared. This solution was stirred with a magnetic agitator for 3 hours. It is STARBURST (registered trademark) in 33.0g of this solution. DIN DORIMA of the 3rd product (Michigan Molecular Institute make) 0.87ml of solutions of a 5, 10, 15, 20-tetrakis-(1-methyl-4-pyridyl)-21H, and 23H-porphin tetra--p-tosylate salt (6.1mg, product made from Aldrich Chemical Corporation) which dissolved in 1.104ml of aqueous solutions and 10ml of water 10% of the weight was added. This mixed liquor was filtered with 0.45micro filter. 0.005 % of the weight of porphyrin colors, 0.3 % of the weight of DIN DORIMA, 83.7 % of the weight of water, 8.4 % of the weight of butyl carbitols, 5.6 % of the weight of glycerol, 2 % of the weight of cyclohexyl pyrrolidinone, 0.032 % of the weight of polyethylene oxide, and DOWICIL (registered trademark) Brown ink containing 0.05 % of the weight was obtained.

[0026] In this way, prepared ink was included in a DESK JET Hewlett Packard (registered trademark) ink jet printer. Xerox 4024 paper (Xerox Corp. make) and Sanyo

KokusakuFX-L A print was formed on paper (Fuji Xerox make). A pattern was undetectable on a print under observation conditions ordinary about each. Macbeth TR927 Optical density of a poor print area measured with a concentration meter was 0.01. Fluorolog 212 When a print put into a sample room of fluorescence spectrometer (product made from SPEX) was irradiated on wavelength of 418 nanometers, light was emitted in strong fluorescence characterized by 648 nanometers and two bands of max 714 nanometers. Contrast excellent in both papers was acquired. About Xerox4024 paper, a ratio to fluorescence intensity (654 nanometers) of a blank paper of fluorescence intensity (648 nanometers) of a print area is 10, and is Sanyo Kokusaku FX-L. About paper, it was 11.7. A print area described Xerox 4024 paper (a wire side) was cut on a sheet of two sheets, one sheet was immersed in water for 2 minutes, this immersed sheet was air-dried at a room temperature for 24 hours, and the water resisting property of a print for which it asked by measuring fluorescence intensity which irradiated both an immersed sheet and a sheet which is not immersed under the same conditions was 92.7% ( $0.89 / 0.96 \times 100$ ).